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(54) Yttrium enriched aluminide coating for superalloys.

(57) A protective coating system for superalloys is described. The coating is an active element enriched aluminide, and can be formed by aluminizing an overlay coated superalloy, wherein during the aluminizing process, aluminum diffuses completely through the overlay coating and into the substrate. The coating system exhibits desirable oxidation resistance and resistance to thermal fatigue cracking, due to the presence of oxygen active elements in the overlay.

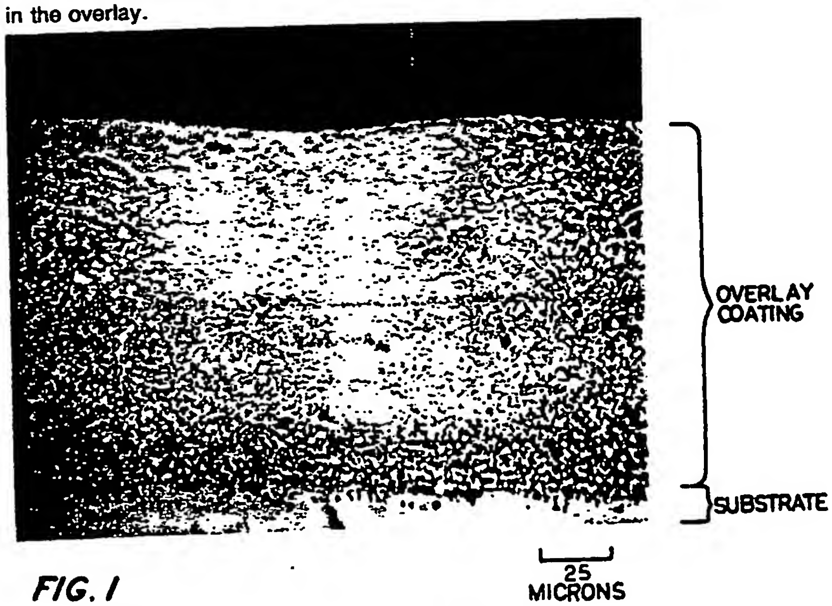

FIG. 1

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The present invention relates to protective coatings for metal substrates. More particularly, the present invention relates to yttrium enriched aluminide coatings for gas turbine engine components.

The superalloys are a class of materials which exhibit desirable mechanical properties at high temperatures. These alloys generally contain major amounts of nickel, cobalt and/or iron either alone or in combination, as their basis material, and alloying additions of elements such as chromium, aluminum, titanium, and the refractory metals. Superalloys have found numerous applications in gas turbine engines.

In most gas turbine applications, it is important to protect the surface of the engine component from oxidation and corrosion degradation, as such attack may materially shorten the useful life of the component, and cause significant performance and safety problems.

Coatings can be used to protect superalloy engine components from oxidation and corrosion. The well known family of coatings commonly referred to as MCrAlY coatings, where M is selected from the group consisting of iron, nickel, cobalt, and various mixtures thereof, can markedly extend the service life of gas turbine engine blades, vanes, and like components. MCrAlY coatings are termed overlay coatings, denoting the fact that they are deposited onto the superalloy surface as an alloy, and do not interact significantly with the substrate during the deposition process or during service use. As is well known in the art, MCrAlY coatings can be applied by various techniques such as physical vapor deposition, sputtering, or plasma spraying. MCrAlY coatings may also include additions of noble metals, hafnium, or silicon, either alone or in combination. They may also include other rare earth elements in combination with or substitution for yttrium. See, e.g., the following US patents which are incorporated by reference: 3,542,530, 3,918 139, 3,928,026, 3,993,454, 4,034,142 and Re. 32, 121.

US patent Re. 32 121 states that MCrAlY coatings are the most effective coatings for protecting superalloys from oxidation and corrosion attack.

Aluminide coatings are also well known in the art as capable of providing oxidation and corrosion protection to superalloys. See, for example, US patent Nos. 3,544,348, 3,961,098, 4,070,507 and 4,132,816.

During the aluminizing process there is significant interaction between the aluminum and the substrate; the substrate chemistry and deposition temperature exert a major influence on coating chemistry, thickness and properties. A disadvantage of aluminide coatings is that in the thicknesses required for optimum oxidation and corrosion resistance, generally taught by the prior art to be about 0.0035 inches, the coatings are brittle and can crack when subjected to the stresses which gas turbine engine blades and vanes typically experience during service operation. These cracks may propagate into the substrate and limit the structural life of the superalloy component; the tendency to crack also results in poor oxidation and corrosion resistance, as discussed in US patent Nos. 3,928,026, 4,246,323, 4,382,976 and Re. 31,339.

Aluminide coatings less than about 0.0035 inches thick may have improved crack resistance, but the oxidation resistance of such thin aluminides is not as good as that of the MCrAlY coatings.

In US patent Nos. 3,873,347 and 4,080,486 an attempt is made to combine the advantages of MCrAlY coatings and aluminide coatings. Therein, an MCrAlY coating, preferably 0.003-0.005 inches thick, is aluminized in a pack cementation process, wherein radially aligned defects in the MCrAlY coating are infiltrated with aluminum diffusing inwardly from the pack mixture. More importantly, a high concentration of aluminum results at the outer surface of the MCrAlY coating, which improves the high temperature oxidation resistance of the coating as compared to the untreated MCrAlY. Both patents state that in laboratory tests, the aluminized MCrAlY coating exhibited improved corrosion resistance, although this is somewhat at variance with the conventional wisdom that aluminum enrichment improves oxidation resistance rather than corrosion resistance.

According to US patent No. Re. 30,995, in order to prevent cracking and spalling of an aluminized MCrAlY coating from the substrate, the aluminum must not diffuse into the substrate; aluminum may diffuse no closer than 0.0005 inches to the MCrAlY/substrate interface. It is also stated that the aluminum content in the aluminized MCrAlY must be less than ten weight percent, in order to achieve the best combination of coating properties.

In US patent No. 3,961,098, an MCr powder is flame sprayed onto a metallic substrate in such a manner that the powder particles are substantially non-molten when they strike the substrate surface. Aluminum is subsequently diffused through the overlay coating, and into the substrate surface. Laboratory tests revealed that the aluminizing step must be conducted so that the final aluminum concentration in the coating is less than weight percent, or else the coating will be brittle, and will have unacceptable corrosion and oxidation resistance.

US patent No. 4,246,323 teaches a process for enriching an MCrAlY coating with aluminum. The processing is conducted so that Al diffuses only into the outer surface of the MCrAlY. The outer, Al rich portion of the coating is reported to be resistant to oxidation degradation, and the inner, unaluminized MCrAlY reportedly has good mechanical properties.

In US patent No. Re. 31,339 an MCrAlY coated superalloy component is aluminized, and then the coated component is hot isostatically pressed. A substantial increase in coating life is reported, which is attributed to the presence of a large reservoir of an aluminum rich phase in the outer portion of the MCrAlY. As in the patents discussed above, the aluminum diffuses only into the MCrAlY outer surface. US patent No. 4,152,223 discloses a process similar to that of US patent No. Re. 31,339, in which an MCrAlY coated superalloy is surrounded by a metallic envelope, and then hot isostatically pressed to close any defects in the MCrAlY coating and to diffuse a portion of the envelope into the overlay. If aluminum foil is used as the envelope, the foil may melt during hot isostatic pressing and form intermetallic compounds with the substrate. It is stated that these compounds may enhance the oxidation resistance of the coating. However, such intermetallics may have an undesired effect on the fatigue strength of the coated component.

In US patent No. 4,382,976, an MCrAlY coated superalloy component is aluminized in a pack process wherein the pressure of the inert carrier gas is cyclicly varied. Aluminum infiltrates radially aligned defects of the overlay, and reacts with the MCrAlY to form various intermetallic, aluminum containing phases. The extent of Al diffusion into the substrate alloy was reported to be significantly less than if the aluminizing were carried out directly on the substrate.

In US patent No. 4,101,713, high energy milled MCrAlY powders are applied to superalloy substrates by flame spray techniques. It is stated that the coated component can be aluminized, whereby aluminum would diffuse into the MCrAlY coating, and if desired, into the substrate material. However, according to US patent No. Re. 30,995 (issued to the same inventor) diffusion of aluminum into the substrate may cause spalling of the MCrAlY coating from the substrate.

Other US patents which disclose aluminized MCrAlY coatings are 3,874,901 and 4,123,595.

In US patent No. 4,005,989 a superalloy component is first aluminized and then an MCrAlY overlay is deposited over the aluminized layer. The two layer coating is heat treated at elevated temperatures, but no information is given as to the results of such heat treatment. The coating was reported to have improved resistance to oxidation degradation compared to the aluminized MCrAlY coatings discussed above.

Other patents which indicate the general state of the art relative to coatings for superalloys include US patent Nos. 3,676,085, 3,928,026, 3,979,273, 3,999,956, 4,109,061, 4,123,594, 4,132,816, 4,198,442, 4,248,940 and 4,371,570.

As the operating conditions for superalloy components become more severe, further improvements are required in oxidation and corrosion resistance, and resistance to thermal mechanical fatigue. As a result, engineers are continually seeking improved coating systems for superalloys. The aforementioned advances in coating technology have markedly improved resistance to oxidation degradation. However, these advances have failed to address what is now viewed as the life limiting property for coated superalloys: resistance to thermal mechanical fatigue cracking.

It is an object of the present invention to provide an improved coating system for superalloys.

Yet another object of the present invention is a low cost coating system for superalloys.

Another object of the present invention is a coating system for superalloys which has improved resistance to oxidation degradation, and improved resistance to thermal mechanical fatigue.

Yet another object of the present invention is a coating system for superalloys which has the oxidation resistance of MCrAlY coatings, and the resistance to thermal mechanical fatigue cracking of thin aluminide coatings.

According to the present invention, a coated gas turbine engine component comprises a superalloy substrate having a thin yttrium enriched aluminide coating thereon. The coating has the oxidation resistance of currently used MCrAlY coatings, and thermal fatigue life which is significantly better than current MCrAlY coatings and equal to that of the best aluminide coatings.

The coating of the present invention may be produced by applying a thin, nominally 0.0015 inch, overlay coating to the surface of the superalloy substrate, and then subjecting the coated component to a pack aluminizing process wherein aluminum from the pack diffuses into and through the coating and into the superalloy substrate.

The resultant invention coating has a duplex microstructure, and is about 0.001 to 0.004 inches thick; the outer zone of the duplex microstructure ranges from between about 0.0005 to about 0.003 inches, and comprises, inter alia, about 20-35 weight percent Al enriched with about 0.2-2.0 weight percent Y. The high Al content in the outer zone provides optimum oxidation resistance, and the presence of Y results in improved alumina scale adherence which reduces the rate of Al depletion from the coating during service operation.

As a result, the coating has better oxidation resistance than current aluminide coatings, and comparable or better oxidation resistance than current MCrAlY coatings. The inner, or diffusion coating zone contains a lesser concentration of aluminum than the outer zone, but a greater concentration of Al than the substrate.

The diffusion zone acts to reduce the rate of crack propagation through the coating and into the substrate. As a result, specimens coated according to the present invention have improved resistance to thermal mechanical fatigue cracking relative to overlay coated specimens, and comparable resistance to thermal mechanical fatigue cracking relative to specimens coated with the most crack resistant aluminides.

According to a preferred embodiment of the invention the overlay coating is an MCrAlY coating consisting essentially of, by weight percent, 20-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni. More preferably, it consists essentially of 30-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni. Most preferably, it consists essentially of about 35 Co, 15 Cr, 11 Al, 2.5 Y, balance Ni.

According to another embodiment, this invention is a superalloy component characterized by a diffusion aluminide coating which also contains small amount of yttrium, silicon and hafnium. The resultant coating has a duplex microstructure, and is about 0.001 to 0.004 inches thick; the outer zone of the duplex microstructure ranges from between about 0.0005 to about 0.003 inches, and comprises about 20-35 weight percent aluminum enriched with about 0.1-5.0 weight percent yttrium, about 0.1-7.0 weight percent silicon and about 0.1-2.0 weight percent hafnium. The high aluminum content in the outer zone provides optimum oxidation resistance, and the presence of yttrium, silicon and hafnium improve the adherence of the alumina scale which forms during high temperature use of the coated component.

The primary advantage of the coating of the present invention is that it combines the desired properties of aluminide coatings and overlay coatings to a degree never before achieved.

Another advantage of the coating of the present invention is that it is easily applied using techniques well known in the art.

The foregoing and other objects, features and advantages of the present invention will become more apparent in the light of the following detailed description of the preferred embodiments thereof as illustrated in the accompanying drawing.

Fig. 1 is a photomicrograph (750X) of an MCrAlY overlay coating useful in producing a coating according to the present invention;

Fig. 2 is a photomicrograph (750X) of the coating according to the present invention; and

Fig. 3 shows comparative oxidation and thermal mechanical fatigue behaviour of several coatings, including the coating of the present invention.

Fig. 4 shows the results of cyclic oxidation tests of several coatings, including the coating of this invention.

The present invention is a diffused, yttrium enriched aluminide coating for superalloys. In one embodiment described below, the coating may be produced by first applying a thin MCrAlY overlay to the surface of the superalloy, and then aluminizing the MCrAlY coated component. The resultant coating microstructure is similar to the microstructure of aluminide coatings, but contains yttrium in sufficient concentrations to markedly improve the coating oxidation resistance. Unlike simple MCrAlY overlay coatings, the coating of the present invention includes a diffusion zone which is produced during the aluminizing step, which, as will be described below, results in the coated component having desirable thermal mechanical fatigue strength.

In another embodiment the coating is a modified diffusion aluminide coating which contains small but effective amounts of yttrium, silicon and hafnium. The coating is produced by first applying a thin overlay coating to the surface of the superalloy, and then aluminizing the overlay coated component. The resultant coating microstructure is similar to the microstructure of aluminide coatings, but contains yttrium, silicon and hafnium in sufficient concentrations to markedly improve the coating oxidation resistance.

The coating has particular utility in protecting superalloy gas turbine engine components from oxidation and corrosion degradation, and has desirable resistance to thermal fatigue. Blades and vanes in the turbine section of such engines are exposed to the most severe operating conditions, and as a result, the coating of the present invention will be most useful in such applications.

The coating of the present invention is best described with reference to Fig. 1 and 2. Fig. 1 is a photomicrograph of an MCrAlY overlay coating approximately 0.001 inches thick, applied to the surface of a nickel base superalloy. As is typical of overlay coatings, the MCrAlY forms a discrete layer on the superalloy surface; there is no observable diffusion zone between the MCrAlY and the substrate. Fig. 2 is a photomicrograph showing the microstructure of the coating of the present invention, etched with a solution of 50 millilitres (ml) lactic acid, 35 ml nitric acid, and 2 ml hydrofluoric acid. The coating shown in Fig. 2 was produced by aluminizing a thin MCrAlY overlay coating similar to the coating of Fig. 1.

Metallographically, it is seen that the coating of the present invention has a duplex microstructure, characterized by an outer zone and inner, diffusion zone between the outer zone and substrate. Electron microprobe microanalysis has indicated that on a typical nickel base superalloy, the outer zone nominally contains, on a weight percent basis, about 20-35 Al, about 0.2-2.0 Y, up to about 40 Co, and about 5-30 Cr,

with the balance nickel. As will be described in further detail below, the final outer zone composition results from the addition of about 10-25 % Al to the preexisting MCrAlY coating composition during the aluminizing process. The diffusion zone contains a lesser concentration of Al than the outer zone, and a greater concentration of Al than the substrate; it also contains elements of the substrate. The diffusion zone also may include (Ni, Co) Al intermetallic compounds, a nickel solid solution, and various Y containing compounds.

While the coating of the present invention may be produced by an overlay coating process followed by a diffusion process, the resultant coating microstructure is metallographically similar to that of many aluminide coatings. Since the coating also includes a significant amount of Y, the coating of the present invention is referred to as an yttrium enriched aluminide.

With the modified diffusion aluminide coating containing yttrium, silicon and hafnium the microstructure is metallurgically similar to that shown in figures 1 and 2. The overlay coating is an NiCoCrAlY coating which also contains silicon and hafnium applied to the surface of a nickel base superalloy. The coating has also a duplex microstructure characterized by an outer zone and an inner diffusion zone. Electron microprobe analysis has indicated that on a typical nickel base superalloy, the outer zone nominally contains on a weight basis, about 20-35 Al, about 0.1 -5.0 Y, about 0.1-7.0 Si, about 0.1-2.0 Hf, about 10-40 Co and about 5-30 Cr, with the balance nickel. The final zone composition results from the addition of about 5-30 % Al to the preexisting overlay coating composition during the aluminizing process.

Fig. 3 presents the Relative Oxidation Life as a function of Relative Thermal Mechanical Fatigue Life for seven coatings applied to a commercially used Hi base superalloy. Relative Oxidation Life is a measure of the time to cause a predetermined amount of oxidation degradation of the substrate; in tests to determine the oxidation life of the coatings, laboratory specimens were cycled between exposures at 2,100°F for 55 minutes and 400°F for 5 minutes. Relative Thermal Mechanical Fatigue Life is a measure of the number of cycles until the test specimen fractures in fatigue. Test specimens were subjected to a constant tensile load while being thermally cycled to induce an additional strain equal to $\alpha\Delta T$, where α is the substrate coefficient of thermal expansion, and ΔT is the temperature range over which the specimen was cycled. The test conditions were chosen to simulate the strain and temperature cycling of a blade in the turbine section of a gas turbine engine.

Referring to Fig. 3, the Plasma Sprayed NiCoCrAlY + Hf + Si overlay is representative of the coating described in US patent No. Re. 32,121. The Electron Beam NiCoCrAlY is representative of the coating described in US patent No. 3,928,026. The MCrAlY over Aluminide coating is representative of the coating described in US patent No. 4,005,989. The coating denoted "Prior Art Aluminized MCrAlY" was a 0.006 inch NiCoCrAlY coating which was aluminized using pack cementation techniques to cause diffusion of Al into the outer 0.002 inches of the overlay.

Aluminide A is representative of a diffusion coating produced by a pack cementation process similar to that described in US patent No. 4,132,816, but with slight modifications to enhance the thermal fatigue resistance of the coated component. The coating denoted "Invention Aluminized MCrAlY" had a microstructure similar to that shown in Fig. 2, and was produced by aluminizing a thin overlay according to the process described below.

As is apparent from Fig. 3, the coating of the present invention exhibits resistance to oxidation degradation which is comparable to the most oxidation resistant coating which was tested. Also, the coating of the present invention exhibits resistance to thermal mechanical fatigue which is comparable to the most crack resistant coating which was tested. Thus a unique and never before achieved combination of properties is achieved by the coating of this invention.

The coating of the present invention can be produced using techniques known in the art. One method is by aluminizing an overlay coated superalloy using pack cementation techniques. As noted above, in the prior art aluminized MCrAlY coatings, the MCrAlY is generally 0.003-0.005 inches thick. Also in the prior art, the aluminizing step is usually carried out to limit the Al content to less than 20 weight percent according to US patent 3,961,098, although US patent No. Re. 30,995 specifies less than 10 weight percent. In the present invention, the overlay is relatively thin: less than about 0.003 inches thick and preferably between about 0.0005 and 0.0015 inches thick. The aluminizing process is carried out so that the resultant Al content in the outer coating zone (Fig. 2) is at least 20%. It is believed that the desirable oxidation resistance of the coating of the present invention is due to the presence of yttrium in the outer coating zone which contains such a high aluminum content. The high Al content provides good resistance to oxidation degradation, und the presence of Y results in improved alumina scale adherence, and a resultant reduced rate of Al depletion from the coating. That the coating of the present invention has improved fatigue properties (Fig.3) when the Al content is greater than 20 % is surprising, and contrary to the teachings of the prior art. See, for example, US patent No. 3,961,098. The favourable resistance to thermal mechanical fatigue cracking is

believed due to the thinness of the coating and the interaction of the inner and outer coating zones. The combined thickness of the outer and inner zones should be about 0.001 to 0.005 inches, preferably about 0.002 to 0.003 inches. If a crack forms in the outer zone, the propagation rate of the crack will be relatively low due to the thinness of the outer zone, in accordance with crack propagation theories of Griffith, discussed in e.g., F. A. Clintock and A. S. Argon, Mechanical Behaviour of Materials, Addison-Wesley, 1966, pp. 194-195. Once the crack reaches the diffusion zone, the crack surfaces will begin to oxidize, because the diffusion zone contains a lesser concentration of Al than the outer zone. As the crack oxidizes, the surfaces of the crack will become rough, and the crack tip will become blunted thereby reducing its propagation rate.

When the diffusion aluminide coating in addition to yttrium, also contains silicon and hafnium, it is believed that the desirable oxidation resistance of the coating of the present invention is not only due to the presence of yttrium but also silicon and hafnium in the outer coating zone which contains the high aluminium content. The presence of silicon and hafnium also results in improved alumina scale adherence.

As noted above, the diffusion zone contains elements of the substrate. Superalloys generally contain refractory elements such as W, Ta, Mo, and Cb for solid solution strengthening, as discussed in US patent No. 4,402,772. During the elevated temperature aluminizing process, these elements tend to migrate into the diffusion zone. Some refractory elements are known to decrease oxidation resistance, and due to their presence in the diffusion zone, the diffusion zone has poorer resistance to oxidation than the outer zone and the substrate. Thus, once the crack reaches the diffusion zone, oxidation of the crack surfaces proceeds at a rate which is more rapid than the rate in either the outer zone or the substrate, thereby significantly decreasing the crack propagation rate.

The MCrAlY coating can be applied by, e.g., plasma spraying, electron beam evaporation, electroplating, sputtering, or slurry deposition. Preferably, the MCrAlY coating is applied by plasma spraying powder having the following composition, on a weight percent basis: 10-40 Co, 5-30 Cr, 5-15 Al, 1-5 Y, with the balance essentially Ni. A more preferred composition range is 20-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni. The most preferred composition is about 35 Co, 15 Cr, 11 Al, 2.5 Y, balance Ni. The plasma spray operation is carried out under conditions whereby the powder particles are substantially molten when they strike the substrate surface.

After the MCrAlY coating has been applied to the surface of the superalloy component, aluminum is diffused completely through the MCrAlY coating and to a significant depth into the superalloy substrate. Preferable, the MCrAlY coated component is aluminized using pack cementation techniques. During the aluminizing process, aluminum reacts with the MCrAlY overlay coating to transform it into an yttrium enriched aluminide coating.

The overlay coating containing silicon and hafnium is applied is applied by plasma spraying powder particles having the following composition, on a weight percent basis: 10-40 Co, 5-30 Cr, 5-15 Al, 0.1-5 Y, 0.1-7 Si, 0.1-2 Hf, balance Ni. A more preferred composition range is 20-24 Co, 12-20 Cr, 10-14 Al, 0.1-3.5 Y, 0.1-7 Si, 0.1-2 Hf, balance Ni. The most preferred composition is about 22 Co, 17 Cr, 12.5 Al, 0.6 Y, 0.4 Si, 0.2 Hf, balance Ni. The combined amounts of yttrium, silicon and hafnium which should be in the overlay coating is between about 0.5 and 9 weight percent. A more preferred range is about 0.5-6 %. Most preferably, the combined yttrium, silicon and hafnium content is about 1.2 %. The plasma spray operation is preferably a vacuum or low pressure plasma spray operation, and powder particles are substantially molten when they strike the substrate surface. See US patent No 4,585 481.

After the overlay coating has been applied to the surface of the superalloy component, aluminum is diffused completely through the overlay coating and into the superalloy substrate. Preferably, the overlay coated component is aluminized using pack cementation techniques. During the aluminizing process, aluminum reacts with the overlay coating to transform the overlay into an aluminide coating enriched with oxygen active elements, i.e., enriched with yttrium, silicon and hafnium.

While pack cementation according to e.g., US patent No 3,544,348 is the preferred method for diffusing aluminum into and through the overlay, aluminum may be diffuses by gas phase deposition, or by, e.g., applying a layer of aluminum (or an alloy thereof) onto the surface of the overlay, and then subjecting the coated component to a heat treatment which will diffuse the aluminum layer through the overlay and into the superalloy substrate. The layer of aluminum can also be deposited by techniques such as electroplating, sputtering, flame spraying, or by slurry techniques, followed by a heat treatment.

The present invention may be better understood through reference to the following example which is meant to be illustrative rather than limiting.

Example I

NiCoCrAlY powder having a nominal particle size range of 5-44 microns and a nominal composition of, on a weight percent basis, 20 Co, 15 Cr, 11.5 Al, 2.5 Y, balance Ni, was plasma sprayed onto the surface of a single crystal Ni-base superalloy having a nominal composition of 10 Cr, 5 Co, 4 W, 1.5 Ti, 12 Ta, 5 Al, balance Ni. The NiCoCrAlY powder was sprayed using a low pressure chamber spray apparatus (Model 005) sold by the Electro Plasma Corporation. The spray apparatus included a sealed chamber in which the specimens were sprayed; the chamber was maintained with an argon atmosphere at a reduced pressure of about 50 millimeters Hg. The plasma spraying was conducted at 50 volts and 1,520 amperes with 85 % Ar-15 % He arc gas. At these conditions, the powder particles were substantially molten when they impacted the superalloy surface. A powder feed rate of 0.3 pounds per minute was used, and the resultant MCrAlY produced was about 0.001 inches thick and was similar to the coating shown in Fig. 1.

After the NiCoCrAlY coating was applied to the superalloy surface, it was glass bead peened at an intensity of .017-.019 inches N, and then the component was aluminized in a pack cementation mixture which contained, on a weight percent basis, 10 CO_2Al_5, 1 Cr, 0.5 NH_4Cl, balance Al_2O_3. The aluminizing process was carried out at 1,875 °F for 3 hours, in an argon atmosphere. The coated component was then given a diffusion heat treatment at 1,975 °F for 4 hours and a precipitation heat treatment at 1,600 °F for 32 hours.

Metallographic examination of the aluminized NiCoCrAlY coated Ni-base superalloy revealed a duplex microstructure, similar to that shown in Fig. 2; the outer zone was about 0.002 inches thick, and the diffusion zone was about 0.001 inches thick. Thus, the combined coating thickness (outer zone plus diffusion zone) was about 0.003 inches thick, and was about 200 greater than the initial MCrAlY coating thickness. Additionally, the diffusion zone extended inward of the outer zone an amount equal to about 50% of the outer zone thickness. Preferably, the diffusion zone thickness is at least about 30 % of the thickness of the outer zone. The nominal composition of the outer zone was determined by electron microprobe microanalysis, which revealed that, on a weight percent basis, the Al concentration was about 24-31, the Y concentration was about 0.3-0.7, the Cr concentration was about 5-18, the Co concentration was less than about 30, with the balance essentially Ni. The diffusion zone contained a lesser Al concentration than the outer zone, and a greater Al concentration than the substrate. In general, the Al concentration in the diffusion zone decreased as a function of depth, although the desirable properties of the coating of the present invention is not dependent on such a depth dependent Al gradient in the diffusion zone. The diffusion zone also contained compounds of the substrate elements.

In oxidation testing conducted at 2,100 °F, the above described coating protected the substrate from degradation for about 1,250 hours, which was comparable to the protection provided by a plasma sprayed NiCoCrAlY + Hf + Si overlay. In thermal mechanical fatigue testing, wherein specimens were subjected to a strain rate of 0.5 % while being alternately heated to a temperature of 800 ° and 1,900 °F, coated nickel base single crystal superalloy test specimens had a life to failure of about 15,000 cycles, which was comparable to the life of a thin aluminide coated specimen (Aluminide B of Fig. 2).

Example II

Tests were conducted to determine whether there was a critical range of MCrAlY compositions which exhibited superior oxidation resistance when aluminized. In these tests, the MCrAlY coatings were applied by low pressure plasma spray techniques, and then peened, aluminized, and heat treated in the manner set forth in Example I. The as-applied MCrAlY coating thickness was about 0.001 inches. The MCrAlY composition evaluated in this example were as follows:

Composition (weight percent)					
Sample	Ni	Co	Cr	Al	Y
A	47	23	18	12	0.0
B	80	0	5	6	9.1
C	0	70	15	12.5	2.5
D	44	23	18	13	1.7
E*	55	10	18	13	3.5
F	43	23	19	13	2.5
G	35	35	15	13	3.1
H	37	35	15	11	2.1

* Also contained 0.7 % Hf

Results of burner rig oxidation testing, where the specimens were heated to about 2,100°F and held for 55 minutes, and then force air cooled for about 5 minutes, are shown in Fig. 4. This figure shows that maximum oxidation resistance was achieved with compositions having a yttrium level between about 2 and 3.5 percent, and a cobalt level between about 20 and 38 percent. Chromium was between about 12-20 percent, aluminum between about 10-14 percent, and the balance was nickel. The need for particular yttrium and cobalt levels are seen on review of the data for samples F, G, and H, which had the best cyclic oxidation life of any of the samples which were tested. The oxidation resistance of the other specimens, which had yttrium and cobalt levels outside of the aforementioned range, were notably inferior, which may be at least partially explained in the following manner: the complete absence of yttrium in sample A resulted in a coating which had poor oxide scale adherence. Yttrium is noted for its beneficial effects on oxide scaled adherence, and the performance of sample A was not unexpected. The very high yttrium level in sample B resulted in a coating having an undesirably low melting point. It also resulted in a coating containing particles enriched in yttrium, which act as sites for internal oxidation (yttrium is readily oxidized). Overlay coatings characterized by the presence of such particles have poor overall oxidation resistance. Sample B also contained no cobalt and too little chromium and aluminum. Sample C shows the effect of no nickel and very high cobalt in the MCrAlY coating, even though yttrium is in the target range. Sample D shows the effect of a low yttrium content even though cobalt is in the target range. And sample E shows the effect of low cobalt even though yttrium is in the target range.

Example III

Cyclic oxidation tests were conducted at 2,100°F to compare the coating life (the number of hours required to oxidize one mil of coating) of an overlay coating having the NiCoCrAlY composition preferred in the practice of this invention with the invention yttrium enriched aluminide coating made with the same NiCoCrAlY composition. The nominal composition of the NiCoCrAlY was Ni-35Co-15Cr-11Y-2.5Y, and the overlay coating was sprayed, peened and then heat treated in the manner set further in Example I. The yttrium enriched aluminide coating was also made in the manner set forth in Example I.

These tests indicated that the coating life of the overlay coating was about 170 hours per mil, while the life of the invention coating was about 410 hours per mil. The invention process improved the coating life nearly 150 %.

Example IV

Powder having a nominal particle size range of 5-44 microns and a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.6 Y, 0.4 Si, 0.2 Hf, balance nickel, was plasma sprayed onto the surface of a nickel base superalloy having a nominal composition of 10 Cr, 5 Co, 4 W, 1.5 Ti, 12 Ta, 5 Al, balance nickel. The powder was sprayed using a low pressure chamber spray apparatus (Model 005) sold by the Electro Plasma Corporation. The spray apparatus included a sealed chamber in which the specimens were sprayed; the chamber was maintained with an argon atmosphere at a reduced pressure of about 50 millimeters Hg. The plasma spraying was conducted at about 50 volts and 1,520 amperes with 85 % Ar-15 % He arc gas. At these conditions, the powder particles were substantially molten when they

impacted the superalloy surface. A powder feed rate of about 0.3 pounds per minute was used, and the resultant overlay produced was about 0.001 inches thick and was similar to the coating shown in Fig. 1.

After the overlay coating was applied to the superalloy surface, it was glass bead peened at an intensity of 0.017-0.019 inches N, and then the component was aluminized in a pack cementation mixture which contained, on a weight percent basis, 10 Co_2Al_5, 1 Cr, 0.5 NH_4Cl, balance Al_2O_3. The aluminizing process was carried out at 1,875 °F for 3 hours, in an argon atmosphere. The coated component was then given a diffusion heat treatment at 1,975 °F for 4 hours and a precipitation heat treatment at 1,600 °F for 32 hours.

Metallographic examination of the aluminized overlay coated nickel base superalloy component revealed a duplex microstructure, similar to that shown in Figure 2; the outer zone was about 0.002 inches thick, and the diffusion zone was about 0.001 inches thick. Thus, the combined coating thickness (outer zone plus diffusion zone) was about 0.003 inches thick, and was about 200 % greater than the initial overlay coating thickness. Additionally, the diffusion zone extended inward of the outer zone an amount equal to about 50 % of the outer zone thickness. Preferably, the diffusion zone thickness is at least about 30 % of the thickness of the outer zone. The nominal composition of the outer zone was determined by electron microprobe microanalysis, which revealed that , on a weight percent basis, the aluminum concentration was about 24-31, the yttrium concentration was about 0.2-0.3, the hafnium concentration was about 0.05-0.15, the silicon concentration was about 0.1-0.2, the chromium concentration was about 5-18, the cobalt concentration was less than about 30, with the balance essentially nickel. The diffusion zone contained a lesser aluminum concentration than the outer zone, and a greater aluminum concentration than the substrate. In general, the aluminum concentration in the diffusion zone decreased as a function of depth, although the desirable properties of the coating of the present invention is not dependent on such an aluminum gradient in the diffusion zone. The diffusion zone also contained compounds of the substrate elements.

In oxidation testing conducted at 2,100 °F, the invention coating protected the substrate from degradation for about 1,250 hours, which was at least equivalent to the protection provided by a plasma sprayed NiCoCrAlY + Hf + Si overlay. In thermal mechanical fatigue testing, wherein specimens were subjected to a strain rate of 0.5 % while being alternately heated to a temperature of 800 ° and 1,900 °F, coated nickel base single crystal superalloy test specimens had a life to failure of about 15,000 cycles, which was at least comparable to the life of a thin aluminide coated specimen (Aluminide B of Fig. 2).

Example V

Powder having a nominal size range of 5-44 microns and a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.6 Y, 0.3 Si, 0.2 Hf balance nickel was plasma sprayed onto the nickel base superalloy described in Example I using the same parameters described in Example I.

The coating was then glass bead peened and aluminized as described in Example I. Oxidation testing at 2,100 °F showed the coating to be protective of the substrate for a period of time of about 1,250 hours.

Example VI

Powder having a nominal particle size of about 5-44 microns and a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.5 Y, 2.2 Si was plasma sprayed onto the nickel base superalloy described in Example I, using the parameters described in Example 1. The coating was also peened and aluminized as described in Example 1. In oxidation testing at 2,100 °F, the coating protected the substrate for about 900 hours.

Example VII

Powder having a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.3 Y, 0.5 Si, 0.6 Ce was sprayed, peened and aluminized as described in Example I. In oxidation tests at 2,100 °F, the coating protected the substrate for a period of time of about 750 hours.

Example VIII

Powder having a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.3 Y, 1.2 Hf was sprayed, peened and aluminized as described in Example I. In oxidation testing at 2,100° F, the coating protected the substrate for a period of time of about 650 hours.

Example IX

Oxidation testing of a simple aluminide coating applied in the manner generally described by Boone et al. in US patent No. 3,544,348 was oxidation tested at 2,100° F. The aluminide coating protected the substrate from oxidation for a period of time of about 375 hours.

Thus, the coatings described in the aforementioned Examples, all being aluminized overlay coatings, had significantly greater resistance to oxidation than the simple aluminide coating of Example IX.

Although the invention has been shown and described with respect to a preferred embodiment thereof, it should be understood by those skilled in the art that other various changes and omissions in the form and detail thereof may be made therein without departing from the spirit and scope of the invention. Even though the Examples discussed above show that yttrium or the combination of yttrium, silicon and hafnium are preferred elements in the overlay coating, other elements which have similar oxygen active properties can be used. These elements include cerium, and the other rare earth elements, as those elements are known to those skilled in the art. At least two of such oxygen active elements should be present in the overlay coating, in an amount which ranges between 0.5 and 9 weight percent.

Although the invention has been shown and described with respect to preferred embodiments thereof, it should be understood by those skilled in the art that other various changes and omissions in the form and detail thereof may be made therein without departing from the scope of the invention.

Claims

1. An article having resistance to oxidation and thermal mechanical fatigue comprising a substrate selected from the group consisting of Ni and Co base superalloys, and a coating diffused with the substrate, wherein the coating has an outer zone and a diffusion zone inward thereof, the outer zone comprising 20-35 weight percent Al and 0.2-2 weight percent Y, and the diffusion zone having a lesser concentration of Al than the outer zone and a greater concentration of Al than the substrate.

2. The article of claim 1 wherein the thickness of said diffusion zone is at least 30% of the thickness of said outer zone.

3. The article of claim 1 wherein the outer zone consisting essentially of, by weight percent, 21-35 Al, 0.2-2 Y, 5-30 Cr, up to 40 Co, with the balance nickel, and the diffusion zone having a lesser concentration of Al than the outer zone and a greater concentration of Al than in the substrate.

4. The article of claim 3, wherein the Al concentration in the diffusion zone decreases as a function of thickness.

5. The article of claim 1, wherein the diffusion zone is less oxidation resistance than the outer zone.

6. The article of claim 5 wherein said Y in said outer zone improves alumina scale adherence, and said diffusion zone reduces the propagation rate of cracks through said coating and into said substrate.

7. A coated nickel or cobalt base superalloy article, wherein the coating is an 0.001-0.004 inch thick yttrium enriched aluminide coating and is characterized by an outer coating zone and a diffusion zone inward thereof, the outer zone containing about 20-35 weight percent aluminum and about 0.2-2.0 weight percent yttrium, and the diffusion zone containing less aluminum than the outer zone and more aluminum that the superalloy article.

8. A coating composition consisting essentially of about, by weight percent, 20-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni.

9. An article having resistance to oxidation and thermal mechanical fatigue comprising a substrate selected from the group consisting of nickel and cobalt base superalloys, and a coating 0.001-0.005 inches thick diffused with the substrate, wherein the coating has an outer zone and a diffusion zone inward thereof, the outer zone consisting essentially of, by weight percent, 21-35 Al, 0.1-5 Y, 0.1-7 Si, 0.1-2 Hf, 5-30 Cr, 10-40 Co, and the balance nickel, and the diffusion zone having a lesser concentration of aluminum than the outer zone.

10. The article of claim 9 wherein the aluminum concentration in the diffusion zone decreases as a function of thickness.

11. A process for producing a coated Ni or Co base superalloy article having resistance to oxidation

and thermal fatigue, comprising the steps of:

(a) applying an MCrAlY overlay coating to the superalloy surface; and

(b) diffusing Al into the MCrAlY coating and into the superalloy substrate so as to form an outer coating zone containing 20-35 weight percent Al and a diffusion zone between the outer zone and the substrate, wherein the diffusion zone has a lesser concentration of Al than the outer zone and a greater concentration of Al than the substrate.

12. The process of claim 11, wherein the MCrAlY overlay is applied to a thickness of between 0.0005 and 0.003 inches.

13. The process of claim 11, wherein the MCrAlY overlay is applied to a thickness of between 0.0005 and 0.0015 inches.

14. The process of claim 11, wherein the combined thickness of the outer zone and diffusion zone is at least about 100 % greater than the initial MCrAlY overlay coating thickness.

15. The process of claim 11, wherein the MCrAlY overlay is applied by plasma spraying powder in such a manner that the powder particles are substantially molten when they strike the superalloy surface.

16. The process of claim 15, wherein said plasma spray powder contains at least 5 weight percent aluminum.

17. The process of claim 16, wherein Al is diffused into the MCrAlY coating by pack cementation techniques.

18. The process for applying an oxidation and thermal fatigue resistant coating to a nickel or cobalt base superalloy article, comprising the steps of

a) applying a 0.0005-0.003 thick NiCoCrAlY coating to the article surface, the coating consisting essentially of, by weight percent, 20-387 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni; and

b) diffusing Al through the NiCoCrAlY coating and into the article so as to form a coating having an outer zone adjacent the surface and a diffusion zone inward thereof, wherein the outer zone contains about 20-35 weight percent Al, and where the diffusion zone contains less Al than the outer zone and more Al than the article, wherein the combined thickness of the outer zone and diffusion zone is about 0.001-0.004 inches.

19. The process of claim 18, wherein the NiCoCrAlY coating consists essentially of about 30-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni.

20. The process of claim 18, wherein the NiCoCrAlY coating consists essentially of about 35 Co, 15 Cr, 11 Al, 2.5 Y, balance Ni.

21. A process for producing a coated nickel or cobalt base superalloy article having resistance to oxidation and thermal fatigue, comprising the step of:

(a) applying a 0.0005-0.003 inch thick overlay coating to the superalloy surface, wherein said overlay coating contains yttrium, silicon and hafnium; and

(b) diffusing aluminum through the overlay coating and into the superalloy substrate so as to form a coating characterized by an outer coating zone containing about 21-35 weight percent aluminum and a diffusion zone between the outer zone and the substrate, wherein the diffusion zone has a lesser concentration of aluminum than the outer zone and the combined thickness of the outer coating zone and the diffusion zone is about 0.001-0.005 inches.

22. The process of claim 21, wherein the overlay is applied to a thickness of between 0.0005 and 0.0015 inches.

23. The process of claim 21, wherein the combined thickness of the outer zone and diffusion zone is at least about 100 % greater than the initial overlay coating thickness.

24. The process of claim 21, wherein the overlay is applied by plasma spraying powder in such a manner that the powder particles are substantially molten when they strike the superalloy surface.

25. The process of claim 21, wherein said plasma spray powder contains at least 5 weight percent aluminum

26. The process of claim 21, wherein the coating thickness is about 0.002-0.003 inches.

27. The process of claim 21, wherein the combined thickness of the coating is about 0.002-0.003 inches.

28. The process of claim 21, wherein the overlay coating is applied by a low pressure plasma spray process.

29. The process of claim 21, wherein the overlay coating is peened before the step of diffusing.

30. The process of claim 21, wherein the overlay coating consists essentially of, by weight percent, 10-40 Co, 5-30 Cr, 5-15 Al, 0.1-5 Y, 0.1-7 Si, 0.1-2 Hf, balance Ni.

31. The process of claim 30, wherein the overlay coating consists essentially of, by weight percent, about 22 Co, 17 Cr, 12.5 Cr, 0.6 Y, 0.4 Si, 0.2 Hf, balance Ni.

32. The process of claim 30, wherein the combined amount of yttrium, silicon and hafnium in the overlay coating is between about 0.5 and 9 percent.

33. The process of claim 30, wherein the combined amount of yttrium, silicon and hafnium in the overlay coating is between about 0.5 and 6 percent.

34. The process of claim 30, wherein the combined amount of yttrium, silicon and hafnium in the overlay coating is between about 1 and 2 percent.

35. The process for producing a coated nickel or cobalt base superalloy article having resistance to oxidation and thermal fatigue, comprising the steps of:

(a) applying a 0.0005-0.003 inch thick overlay coating to the superalloy surface, wherein said overlay coating contains at least two oxygen active elements in a combined amount between about 0.5 and 9 weight percent; and

(6) diffusing aluminum through the overlay coating and into the superalloy substrate so as to form a coating characterized by an outer coating zone containing about 21-35 weight percent aluminum and a diffusion zone between the outer zone and the substrate, wherein the diffusion zone has a lesser concentration of aluminum than the outer zone and the combined thickness of the outer coating zone and the diffusion zone is about 0.001-0.005 inches.

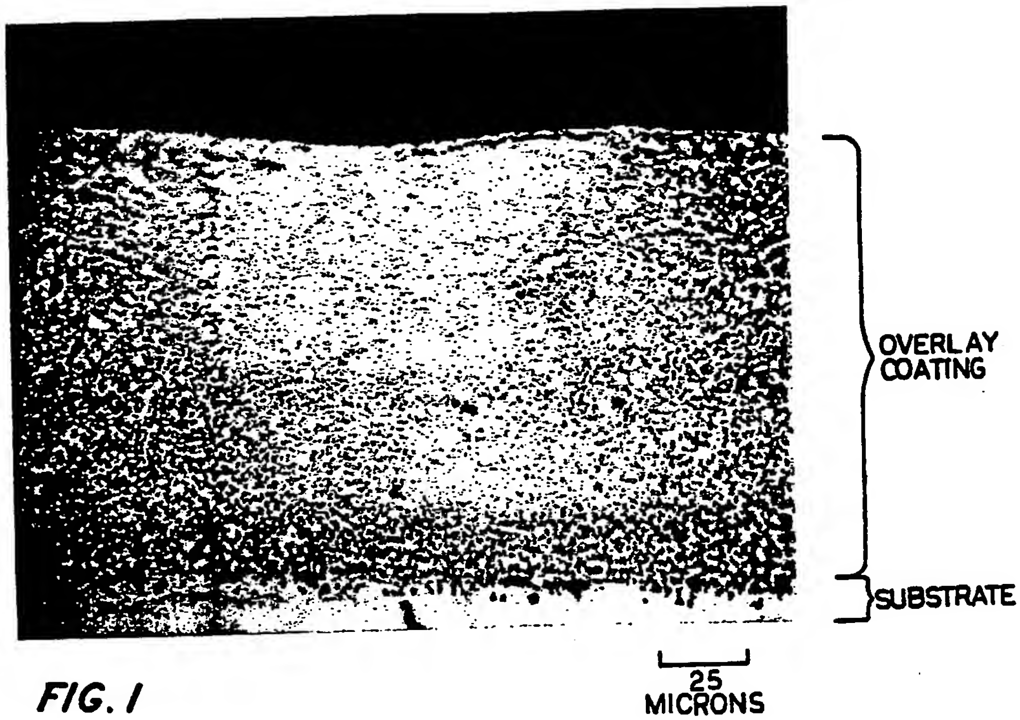

OVERLAY
COATING
SUBSTRATE
25
MICRONS

FIG. 1

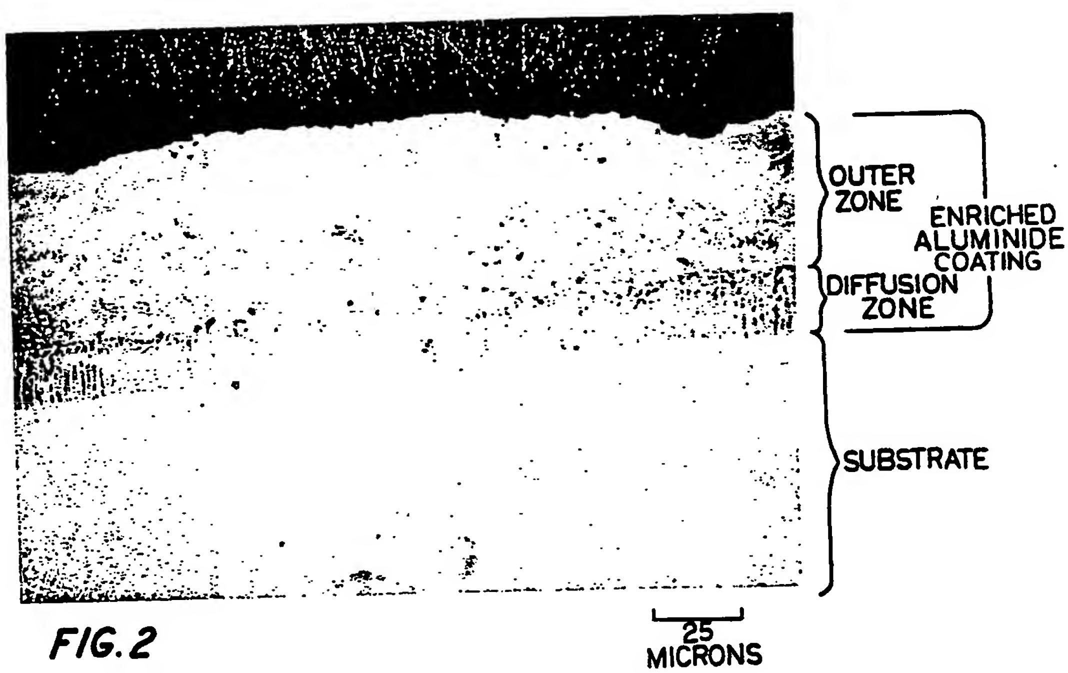

OUTER
ZONE
ENRICHED
ALUMINIDE
COATING
DIFFUSION
ZONE
SUBSTRATE
25
MICRONS

FIG. 2

FIG. 3

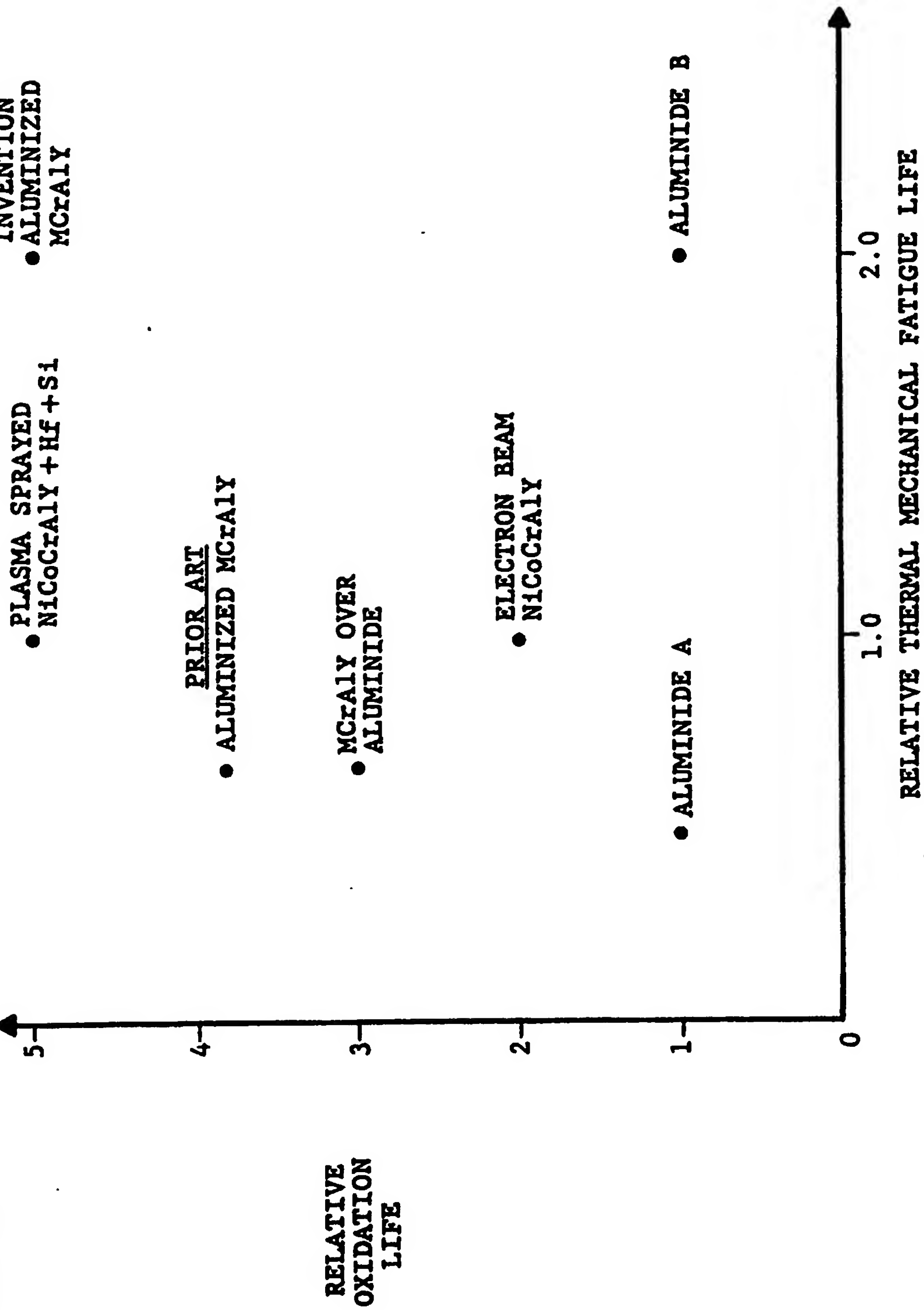
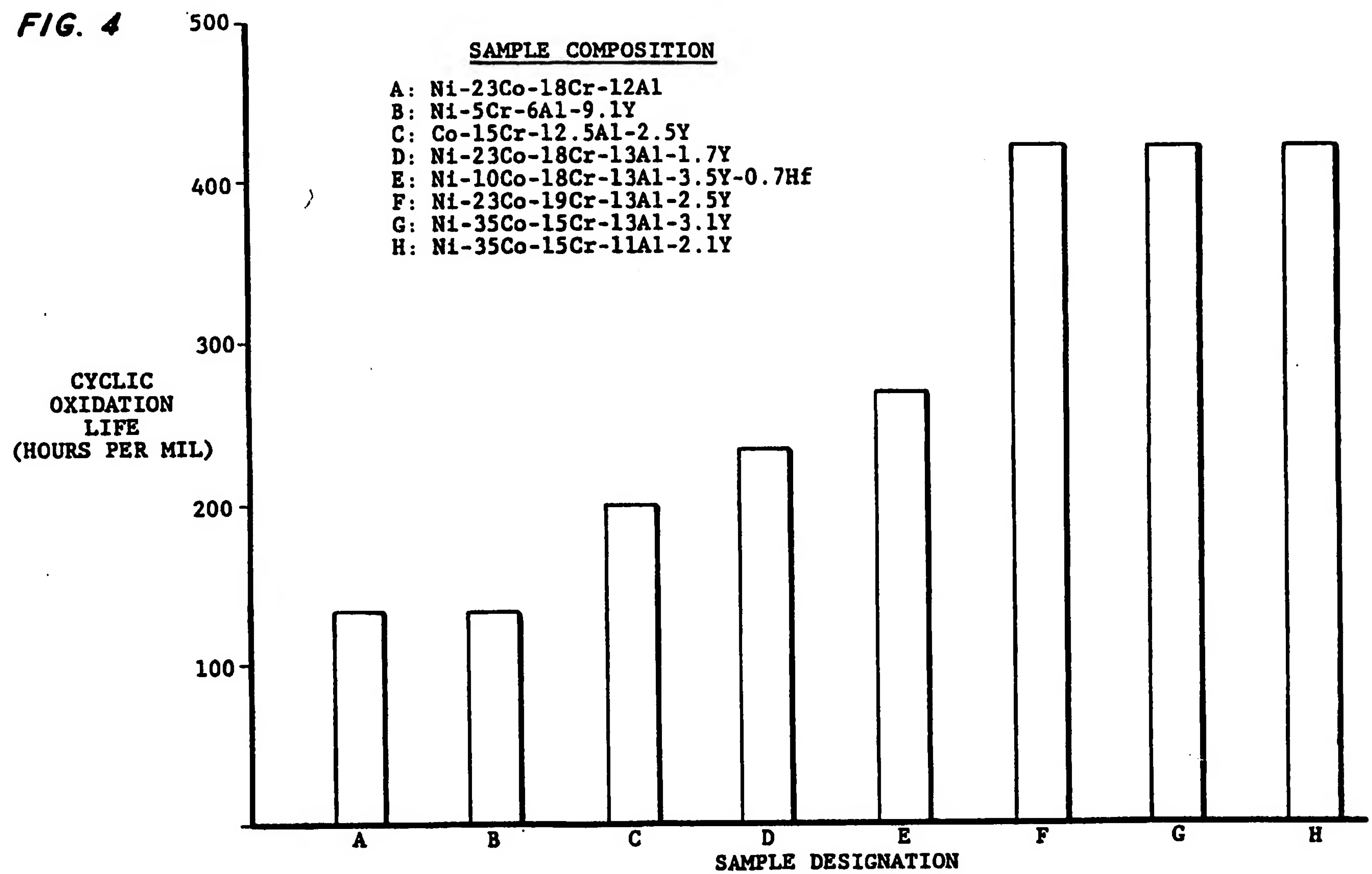

RELATIVE OXIDATION LIFE
RELATIVE THERMAL MECHANICAL FATIGUE LIFE
0
1
2
3
4
5
1.0
2.0
PLASMA SPRAYED NiCoCrAlY + Hf + Si
INVENTION ALUMINIZED MCrAlY
PRIOR ART ALUMINIZED MCrAlY
MCrAlY OVER ALUMINIDE
ELECTRON BEAM NiCoCrAlY
ALUMINIDE A
ALUMINIDE B

FIG. 4



500
400
300
200
100
CYCLIC
OXIDATION
LIFE
(HOURS PER MIL)
SAMPLE COMPOSITION
A: Ni-23Co-18Cr-12Al
B: Ni-5Cr-6Al-9.1Y
C: Co-15Cr-12.5Al-2.5Y
D: Ni-23Co-18Cr-13Al-1.7Y
E: Ni-10Co-18Cr-13Al-3.5Y-0.7Hf
F: Ni-23Co-19Cr-13Al-2.5Y
G: Ni-35Co-15Cr-13Al-3.1Y
H: Ni-35Co-15Cr-11Al-2.1Y
A
B
C
D
E
F
G
H
SAMPLE DESIGNATION

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 63 0218

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A,D	FR-A-2 226 483 (GENERAL ELECTRICAL CO.) * Claims 1,5,6,12; figure 4; page 4, lines 11-14; page 6, lines 1-11 *	1,3,4,11,17	C 23 C 10/02 C 23 C 10/48
A	EP-A-0 024 802 (THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND WHITEHALL) * Claims 1,2,3,5,9; page 3, lines 22-24; page 4, lines 20-23; page 5, line 1 *	1,11,15,17	
A	METAL PROGRESS, vol. 106, no. 3, August 1974, pages 66-68, American Society for Metals, Metal Park, Ohio, US; M.A. GEDWILL et al.: "Aluminized alloy boosts turbine blade life" * Page 66, right-hand column, lines 3-14; page 67, left-hand column, lines 26-30 *	1,11,15,17	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A,D	FR-A-2 223 478 (GENERAL ELECTRIC CO.) * Claims 1,5,6; page 5, lines 18-23 *	1,4,11,12,17	C 23 C
A	US-A-3 849 865 (M.A. GEDWILL) * Claims 1-10 *	11	
A	FR-A-2 503 829 (CREUSOT-LOIRE) * Claims 1,4; page 4, lines 13-32; figure 1 *	1	
A	GB-A-2 009 251 (ROLLS-ROYCE) * Page 1, lines 30-38; page 2, lines 14-19; page 3, lines 6-12; claims 1-16 *	1,11,12,15,17	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05-06-1990	ELSEN D.B.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document